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Vanadium oxide - carbon nanotube composite electrodes for use in secondary lithium batteries

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Single-wall carbon nanotubes were used to form the electronically conducting network in lithium intercalation electrodes that incorporated vanadium oxide aerogels as the active material. Sol-gel methods were developed which integrated the nanotubes with V_2O_5 aerogel synthesis. The similarities in morphology and dimensional scale for the nanotubes and V_2O_5 ribbons enabled excellent electrical contact to be made between the two phases without seriously affecting the aerogel nanostructure. Intimate contact was established between the two phases at the nanodimensional level while the high pore volume of the aerogel provided electrolyte access throughout the composite material. The electrodes exhibited specific capacities in excess of 400 mAh/g at high discharge rates and retained this level of capacity on cycling.

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Introduction

Intercalation electrode materials for lithium-ion batteries have been widely investigated for some two decades.[1-3] Layered hosts and three-dimensional framework solids have largely dominated the field and various materials systems have been developed for the commercial battery market. An interesting variation to this work, which has received much less attention, is the use of amorphous materials as insertion electrodes.[3] For these solids, sol-gel chemistry is particularly convenient as methods for synthesizing non-crystalline and metastable transition metal oxides have been established.[4,5] Although a number of sol-gel based systems have been prepared and their electrochemical properties investigated,[6-10] sol-gel based vanadium oxide has clearly received the most interest.[11,12] An important direction to this work has been to use the sol-gel process to control the microstructure of the vanadium oxide. Based on processing procedures and drying methods, one can produce sol-gel derived materials as xerogels or aerogels.[13] The latter are mesoporous materials in which a continuous, nanometer-scale solid phase forms a highly porous three-dimensional network with high surface area. The vanadium oxide aerogels, produced by either supercritical drying or ambient drying methods,[14-17] are particularly fascinating because their specific capacity for lithium is greater than that of either vanadium oxide xerogels or crystalline V_2O_5.[18] The aerogel materials hold considerable promise for battery applications as specific capacities in excess of 300 mAh/g have been reported for C/4 discharge rate.[19]

The intercalation electrodes used for lithium batteries are composite structures consisting of the active intercalation material, an electronic conductor and a polymer binder.[20, 21] The electronic conductor of choice is carbon black. Although carbon black materials possess a fine particle size, when dried from suspension they form aggregates that may be hundreds of nanometers in diameter. In a standard composite electrode incorporating $LiCoO_2$ as the active material, the carbon black aggregates fill the void spaces between the packed, micrometer-size particles of $LiCoO_2$.[22] The addition of metal fibers to such standard electrodes has produced some improvements in performance.[23]

The unique morphology of vanadium oxide aerogels raises the intriguing question of whether carbon black is the best medium for establishing an electronically conducting network for intercalation electrodes based on this material. In the few studies that have explored this question, the electrochemical characteristics appear to be dependent upon the nature of the electrode. The use of 'sticky carbon' as an electrode provides excellent electrical contact to the submicron particles of the aerogel and, because the pore-solid nanostructure of the aerogel is preserved in this electrode, electrolyte access to the entire particle occurs through the mesoporous network.[24] The voltammograms obtained using this electrode are dominated by a capacitive response, the magnitude of which indicates a pseudocapacitance, in contrast to the characteristic intercalation behavior observed for composite electrodes. A study using nickel fibers as the conductive substrate for vanadium oxide aerogel films demonstrated that high intercalation rates are possible.[25] The nanometer-scale solid phase of the aerogel reduces the lithium diffusion path and avoids diffusion limitations while good electronic conduction is maintained by contact

through the nickel fibers. These electrodes are reported to have specific energies above 100 Wh/kg at high discharge rates and specific powers of nearly 6 MW/kg. It is important to mention that in both studies the mass loading of the active vanadium oxide aerogel was less than 100 $\mu g/cm^2$.

The present paper describes the use of single wall carbon nanotubes (SWNT's) as the conductive additive for intercalation electrodes which incorporate vanadium oxide aerogels as the active material. The carbon nanotubes have a similar morphological character and dimensional scale as the vanadium oxide ribbons that compose the aerogel.[26] Thus, there is an opportunity to exploit the high conductivity of the SWNT's ($\approx 10^4$ S/cm) and have them provide electronic conduction without blocking electrolyte access to the active material. In contrast, traditional composite electrodes are characterized by the aggregation of carbon black particles because of the volume fraction of additive required to reach the percolation threshold. While SWNT's have been investigated as anodes for lithium batteries,[27] we are unaware of their incorporation in cathode structures. The low density of the SWNT's (≈ 1.33 g/cm^3)[26] enables one to prepare these electrodes using low weight fractions of conductor, and comparisons can be made between electrodes containing SWNT's and carbon black. Based on the metal fiber experiments,[23,25] one would expect the V_2O_5 aerogel/SWNT electrodes to have good performance at high discharge rates and this is indeed observed. In addition, results show that the composite electrodes do not exhibit capacity loss on cycling.

Experimental

Two types of intercalation electrodes were prepared in which the active material was the vanadium oxide aerogel. A standard, reversible lithium electrode was prepared using Ketjen Black (KJB, from Akzo Nobel) as the conductive additive, while the second type incorporated SWNT's. For both types of electrodes, the vanadium oxide aerogel component was prepared using sol-gel synthesis in combination with an ambient drying approach.[17] Vanadium oxide gels were prepared by adding a solution of 1.8 cm^3 H$_2$O and 6 cm^3 of acetone to 0.6 cm^3 of vanadyl triisopropoxide, VO(OC$_3$H$_7$)$_3$ (Alfa; purity > 99%). Gelation occurred within 30 seconds, and these 'wet gels' were then aged for 3 days at room temperature in sealed tubes. After removal from the tubes, the samples were washed repeatedly in anhydrous acetone (Fisher Scientific) and then washed several times in cyclohexane (Fisher Scientific). Ambient drying of cyclohexane, or other nonpolar solvents, from the wet gel leads to an aerogel-like material (termed an 'ambigel').[17] The ambigel was heated in air at 125°C to remove residual solvent. For preparing standard electrodes, the V$_2$O$_5$ was ground to a fine powder, suspended in cyclohexane and combined with KJB (5, 9, and 17 wt% as described below) and poly(vinylidine fluoride) (PVDF from Aldrich). The addition of propylene carbonate (Aldrich; 99.7% with 70 ppm water content) to this mixture caused a slurry to form at the bottom of the container. The slurry was spread on a high-purity stainless steel mesh and dried under vacuum (10^{-3} Torr) at 240°C (1 hr). The mass loading of the vanadium oxide aerogel on the mesh was 1 to 2 mg V$_2$O$_5$/cm^2.

The key feature in preparing the V_2O_5/SWNT composite electrodes was to use the suspension of SWNT's as the source of acetone in preparing the gel. The SWNT's were received suspended in toluene.[28] To suspend them in acetone, the SWNT/toluene suspension was heated in a silicon bath at 130°C, exceeding the boiling point of toluene. As the toluene evaporated, acetone was added to keep the SWNT's suspended at all times. This procedure was repeated until all the toluene was replaced. It is important to note that some agglomeration of SWNT's occurred upon adding acetone, however, the SWNT's remained suspended and did not sediment over weeks. This suspension was then combined with the requisite amounts of vanadium alkoxide precursor and water to produce a wet gel. Although the volume of acetone used in preparing the vanadium oxide gel remained the same (6 cm^3), the concentration of SWNT's suspended in acetone was varied. In this way, it was possible to prepare V_2O_5/SWNT composites in which the weight percentage of SWNT was controlled from 5 to 17 weight percent. The same gelation, drying, slurry preparation and cathode fabrication procedures were used for the V_2O_5/SWNT composites as with the standard electrodes containing KJB as described above.

Electrochemical measurements were made using three-electrode cells filled with 1 M LiClO$_4$ (Aldrich) in anhydrous propylene carbonate. The LiClO$_4$ was dried by heating under vacuum at 145°C for 4 hours. Lithium counter and reference electrodes were prepared by scraping lithium foil (Alfa) with a razor blade to expose a fresh surface. All cell preparation and testing were conducted in an argon-filled glove box (O$_2$ < 0.5 ppm;

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H_2O < 1ppm). Galvanostatic and cyclic voltammetry experiments were carried out using a computer controlled PAR 273A potentiostat/galvanostat.

The electrical resistance for both types of intercalation electrodes was measured at room temperature. Samples were prepared by spraying the slurries, with an airbrush, onto glass substrates (1 cm^2 squares) which had been pre-electroded with silver paste. The weight of material deposited on the substrate was kept constant at approximately 1 mg for each sample. This approach offers a qualitative means of comparing the electrically conducting networks developed by the SWNT and KJB additives. Two-lead complex impedance measurements (EG&G 6310 Frequency Analyzer) were made on samples in the same 1 cm^2 configuration. The values are reported as a sheet resistance (Ω/sq).

Microstructural characterization was carried out using gas adsorption measurements (Micromeritics ASAP 2010) and transmission electron microscopy (JEOL 200 CX). In order to determine the influence of electrode preparation methods on morphology, the V_2O_5, V_2O_5/SWNT and V_2O_5/KJB materials were subjected to the same conditions as those used in preparing the intercalation electrodes. Thus, the powder samples were immersed in propylene carbonate and then heated at 240°C in air. Upon cooling to room temperature, the powders were loaded into sample measurement tubes and degassed (150°C under vacuum) in accordance with standard gas adsorption measurement procedures. TEM samples were prepared by dropping a dilute suspension of powder, suspended in cyclohexane, onto copper grids (Ted Pella).

Results and Discussion

Microstructural Characterization

TEM images of the V_2O_5 ambigel, SWNT's, and the V_2O_5/SWNT composite are shown in Fig. 1. Sol-gel derived vanadium oxide exhibits a characteristic ribbon morphology.[11,15] As shown in Fig. 1a, the ribbons, 1-5 nm in width, aggregate into fibers that are approximately 20 to 30 nm wide. The SWNT's used in this study (Fig. 1b) consist of bundles of nanotubes in which the characteristic bundle diameter is on the order of 10 nm.[26] The presence of nanotubes within the 10 nm diameter bundles is indicated by the parallel lines which run along the length of the bundle (see Fig. 1b).[26] The intimate contact established between the two phases in the composite electrode is shown in Fig. 1c. The SWNT's are well dispersed within the V_2O_5 ribbons and in some instances are intertwined with them.

The most striking feature about the composite is that contact between the two phases is established at the nanodimensional level and that this contact occurs at multiple points along the ribbons. This type of morphology is substantially different from that of traditional electrodes where micrometer-size clusters, which are formed from the aggregation of active material particles, make contact with aggregates of carbon black and PVDF particles.[21] The TEM image in Fig. 1c indicates that while the SWNT bundle morphology is maintained, the V_2O_5 ribbons have agglomerated. As was proposed for metal fibers,[25] it is possible that the presence of the solid phase in the sol lowers the interfacial energy so that gelation occurs preferentially on the SWNT's, leading to

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aggregation. Another possibility is that the SWNT's offer potential sites for V^{4+} to exist; the presence of V^{4+} is critical in the vanadium oxide gelation mechansim.[29,30]

Gas adsorption measurements provide further insight concerning the morphology of the electrodes tested in this study (see Table I). The addition of SWNT's to the electrode leads to a slight decrease in pore volume and average pore diameter. The fact that there is relatively little effect on surface area is likely due to the fact that SWNT's possess a significant surface area by themselves.[31] Perhaps the more significant point to be made is that the V_2O_5/SWNT intercalation electrode effectively retains the pore volume of the initial V_2O_5 aerogel. Also indicated in Table I is that V_2O_5/KJB electrodes possess a comparable level of pore volume as that of the V_2O_5/SWNT materials. The significant level of pore volume, coupled with the 20 to 30 nm pore dimensions, ensures electrolyte access throughout the electrode. The ability for the electrolyte to readily access the solid phase is an important microstructural feature for aerogel-based intercalation electrodes.[32]

A final point of interest concerns the stability of the nanodimensional pores in the aerogel. A commonly voiced concern in using nanoporous aerogels is the possibility that immersion in the electrolyte will lead to pore collapse from capillary forces, thus negating the high surface area and pore volume of the material. It appears that vanadium oxide aerogels do not experience such an effect. As shown in Table I, the properties of pristine vanadium oxide ambigel after immersion in propylene carbonate are virtually identical to the characteristics of comparable samples which have not been immersed.[17,24] The fact that the aerogel morphology is unaffected by exposure to the organic electrolyte is an

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important consideration if these materials are to be viable electrodes for lithium secondary batteries.

Electrical resistance measurements

Electrical resistance measurements are intended to provide a qualitative comparison of the effectiveness of the macroscopic conducting networks developed from the SWNT and KJB additions. The electrical resistance varies considerably depending on the amount and type of conductive additive (Table II). As expected, if there is no conductive additive, the sheet resistance for the V_2O_5 aerogel sample is relatively high (600,000 Ω/sq). Regardless of the type of additive, this value decreases as the amount of conductive additive increases. Moreover, the complex impedance measurements consist of a single point on the real axis, indicating that electronic conduction dominates. It is evident, however, that for equal weight fractions of conductive additive (i.e. KJB or SWNT's), the sheet resistance is lower for the composites containing SWNT's. For example, the sheet resistance for the 17 wt% SWNT composite sample is more than four times lower (700 Ω/sq) than the 17 wt% KJB composite (3,400 Ω/sq). Moreover, substantially less SWNT is required to reach the sheet resistance values obtained with the KJB additive. Thus, the 9 wt% SWNT composite material has approximately the same sheet resistance as that of the 17 wt% KJB composite. It is believed that the nanotube morphology, bundles of nanotubes that are many micrometers in length, is more conducive for 'wiring' the aerogel electrode structure. That is, the nanotubes lead to the

development of a more effective electronically conducting network than one based on discrete particles of carbon black.

Electrochemical characterization

The electrochemical experiments reported here addressed three different types of questions. The first question was the extent to which the SWNT's contributed to the capacity. The second question was whether these electrodes might retain their excellent capacity at high discharge rates. Although prior work had shown that lithium capacities in excess of 300 mAh/g were possible at rates of C/4,[19] V_2O_5/SWNT composite electrodes might be capable of higher rates because they retain the high pore volume and pore size distribution of the parent vanadium oxide aerogel. The final question addressed by these experiments was whether these composite electrodes would retain high capacity on cycling. SWNT bundles exhibit high strength and stiffness,[33] however, they also exhibit voltage induced strains[34] which, with the rigors of cycling, could influence electrical contact within the electrode itself as well as to the current collector.

Cyclic voltammetry was used to analyze the active voltage range for both a SWNT electrode and the V_2O_5/SWNT(17 wt%) composite (Figure 2). Well defined reduction and oxidation peaks occur at 2.4 and 2.8 Volts, respectively, for the V_2O_5/SWNT(17 wt%) electrode. In contrast, the current response over the entire range is negligible for the SWNT electrode. This result establishes that SWNT's are relatively inactive electrochemically from 4 to 1.5 Volts and do not contribute to the capacity of the

V_2O_5/SWNT intercalation electrodes. This behavior is consistent with reported literature indicating that lithium reacts with SWNT's at voltages less than 1.5V.[27]

In the rate capability experiments, the specific discharge capacity (mAh/g) was measured as a function of specific current (mA/g) for both V_2O_5/SWNT and V_2O_5/KJB intercalation electrodes. Three different weight fractions of the conductive additives were compared, 5, 9 and 17 wt%. The data (Table III) display an unexpected trend at the higher discharge rates. At relatively low specific current (112 mA/g), the specific capacities for the nanotube and carbon black composite electrodes are comparable for the same amounts of conductive additive. The 9 and 17 wt% are quite similar to one another, with the 5 wt% a bit lower. At these low discharge rates, the kinetic limitations are relatively minor and the high capacity values reported for V_2O_5 aerogels ($\sim$ 450 mAh/g) are obtained with both types of intercalation electrodes containing either 9 or 17 wt% additive. The specific capacities measured at 112 mA/g agree reasonably well with the highest values reported by Coustier et al.[19] At higher specific currents (560 mA/g), differences begin to appear with respect to the amount and type of conductive additive. The specific capacities for the V_2O_5/SWNT electrodes are consistently higher than the corresponding V_2O_5/KJB electrodes of the same weight fraction of additive. At rates of 1120 mA/g (2C), the results show that V_2O_5/SWNT electrodes containing lower amounts of nanotubes exceed the performance of KJB, i.e., the specific capacity of the 9 wt% SWNT composite is greater than that of 17 wt% KJB composite. At the highest rates tested in this study, 2800 mA/g (5C), the specific capacity for the V_2O_5/SWNT(17 wt%) intercalation electrode is approximately twice as large as that of the V_2O_5/KJB(17 wt%)

material (296 and 155 mAh/g, respectively). Galvanostatic discharge curves comparing the 17 wt% SWNT and KJB composite electrodes are shown in Figure 3 for the highest and lowest specific currents investigated. These curves show that the V_2O_5/SWNT electrode retains high capacity at the high discharge rates. Figure 4 illustrates two of the main features of the discharge rate study. At lower discharge rates, comparable values of specific capacity are obtained for both types of electrodes. At the higher rates, the electrodes containing carbon nanotubes exhibit substantially higher capacity with the 9wt% SWNT electrode outperforming the 17 wt% KJB electrode.

The results shown here are quite interesting in that there are no dramatic differences in the basic morphology for each type of electrode. Although there is the prospect of having occluded surfaces, the fact that the pore volume is not substantially different for the various electrodes means that electrolyte access is expected to be comparable for both types of electrodes. It would seem then that the electronically conducting network and the nature of the contact between the conductive component and the vanadium oxide phase must be an important consideration for achieving high rate capability. The macroscopic conductivity measurements (Table II) offer some explanation; higher discharge rate capability is correlated with the measured conductivity. Electrodes prepared with carbon nanotubes as the conductive network exhibit substantially higher conductivity (by at least a factor of 4) compared to electrodes containing the same weight fraction of the KJB additive. However, at the higher discharge rates, the results suggest that an additional factor must contribute because V_2O_5/SWNT composite electrodes with lower macroscopic conductivity exhibit better discharge rate

characteristics than the more conductive V_2O_5/KJB electrodes. That factor may be the nature of the contact between the two components. SWNT's may be better suited to "wiring" the porous aerogel morphology than carbon black aggregates. The intimate contact developed at multiple locations between the V_2O_5 ribbons and SWNT's at the nanometer level (Fig. 1) must be beneficial for retaining the high capacity of the vanadium oxide aerogel at high discharge rates. It therefore seems that the nanostructure of the aerogel-based intercalation electrode becomes an influential factor primarily at the higher discharge rates.

Galvanostatic cycling experiments were carried out in three-electrode cells which were discharged and charged between 4.0 and 1.5 V at rates of 560 mAh/g and 280 mAh/g, respectively. A 15 minute 4.0 V potentiostatic hold was used at the end of each galvanostatic charging step. The results for the V_2O_5/SWNT(17 wt%) electrode are shown in Figure 5. In these 20 cycle tests, the discharge capacity for each cell exhibited a value in excess of 400 mAh/g with no apparent capacity loss during cycling. In contrast, a prior study which used KJB as the conductive additive to the vanadium oxide aerogel reported a capacity loss between 0.195 and 0.40% per cycle.[35] These initial results with the V_2O_5/SWNT composite electrode lead to the intriguing question of whether the incorporation of carbon nanotubes effectively prevents capacity loss during cycling. From a microstructural standpoint, the nanotubes establish excellent electrical contact without impeding electrolyte access to the mesoporous aerogel architecture. Moreover, it is likely that the mechanical integrity of the SWNT network is superior to one composed of aggregated carbon particles since carbon nanotubes are noted for their high mechanical

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strength, high modulus and dimensional stability.[34] This suggests that the SWNT's may mechanically reinforce the electrode structure, enhance electrode integrity during cycling and ensure that intimate electrical contact with the vanadium oxide aerogel phase is not disrupted. More detailed studies of cell cycling behavior are in progress.

Conclusions

Single-wall carbon nanotubes have been incorporated as the conductive additive in lithium intercalation electrodes that use vanadium oxide aerogels as the active material. By integrating the nanotubes as part of the sol-gel chemistry, uniform materials are prepared with controlled weight fractions and electrode loadings in the mg/cm^2 range. The similarity in morphology and dimensional scale for the SWNT's and V_2O_5 ribbons leads to a very different electrode microstructure as compared to traditional intercalation electrodes. The V_2O_5/SWNT composite material possesses a high pore volume that ensures electrolyte access throughout the electrode, while contact between the two phases is established at the nanometer level, and occurs at multiple points along the V_2O_5 ribbons. The V_2O_5/SWNT electrode retains high specific capacity at high discharge rate; this behavior is attributed to the fact that the electronically conducting network developed from the SWNT's is more effective than one based on carbon black. A second interesting property is that the V_2O_5/SWNT electrodes exhibit no apparent capacity loss on cycling. This characteristic may be related to the excellent mechanical properties of the SWNT's and the prospect that the nanotubes reinforce the electrode structure.

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35. It should be noted that in the work reported in Reference 19, electrodes were prepared by a different route which led to a much denser composite electrode.

Table I. Morphology of vanadium oxide aerogel electrodes

Sample	Surface area (m^2/g)	Avg. pore diameter (nm)	Pore volume (cm^3/g)
V_2O_5 ambigel	132	29.5	0.99
V_2O_5/SWNT (5 wt%)	150	20.6	0.76
V_2O_5/SWNT (17 wt%)	121	18.9	0.6
V_2O_5/KJB (17 wt%) *	176	-	0.85
SWNT (from ref. 31)	285/350	-	-

*The contribution from pores < 5 nm diameter has been omitted for this sample to provide a more relevant comparison.

Table II. Sheet resistance measurements of vanadium oxide aerogel electrodes

Electrode	Ω/square
V_2O_5 ambigel	600×10^3
V_2O_5/SWNT (5 wt%)	15.5×10^3
V_2O_5/SWNT (9 wt%)	4.2×10^3
V_2O_5/SWNT (17 wt%)	700
V_2O_5/KJB (5 wt%)	69.6×10^3
V_2O_5/KJB (9 wt%)	8.0×10^3
V_2O_5/KJB (17 wt%)	3.4×10^3
KJB	2×10^3
SWNT	7

Table III. Specific capacities as a function of specific current for intercalation electrodes incorporating V_2O_5 aerogels

Specific current (mA/g)	Specific capacities (mAh/g)				
	V_2O_5/KJB		V_2O_5/SWNT		
	9 wt%	17 wt%	5 wt%	9 wt%	17 wt%
112	425	452	382	449	452
560	326	382	314	373	418
1120	227	323	280	342	395
2800	85	155	210	257	296

Figure captions

Figure 1. TEM images for the following materials:
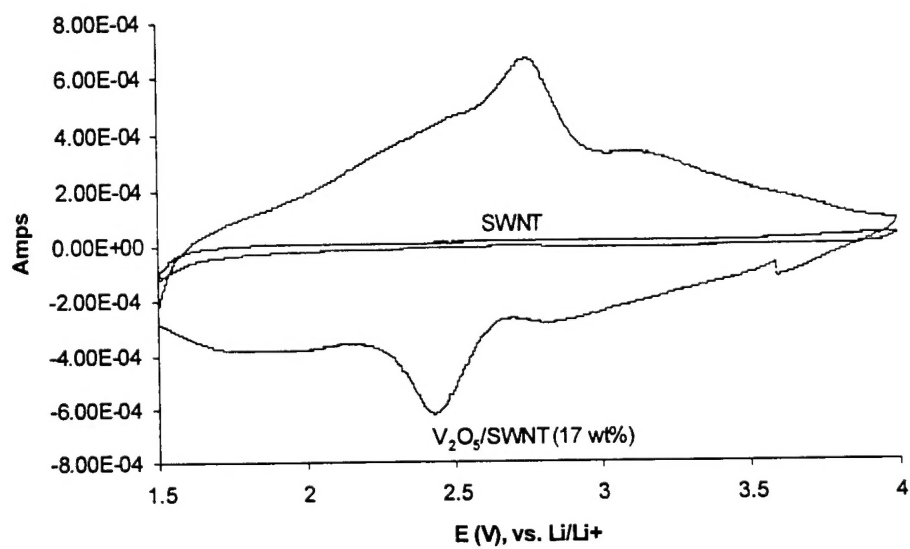(a) vanadium oxide ambigel; (b) SWNT's; (c) V_2O_5/SWNT composite electrode.

Figure 2. Voltammograms for SWNT's and the V_2O_5/SWNT(17 wt%) composite electrode. The sweep rate was 0.1 mV/s and the electrolyte was 1.0 M $LiClO_4$ in propylene carbonate. The mass loading was 1 mg/cm^2 for each electrode.
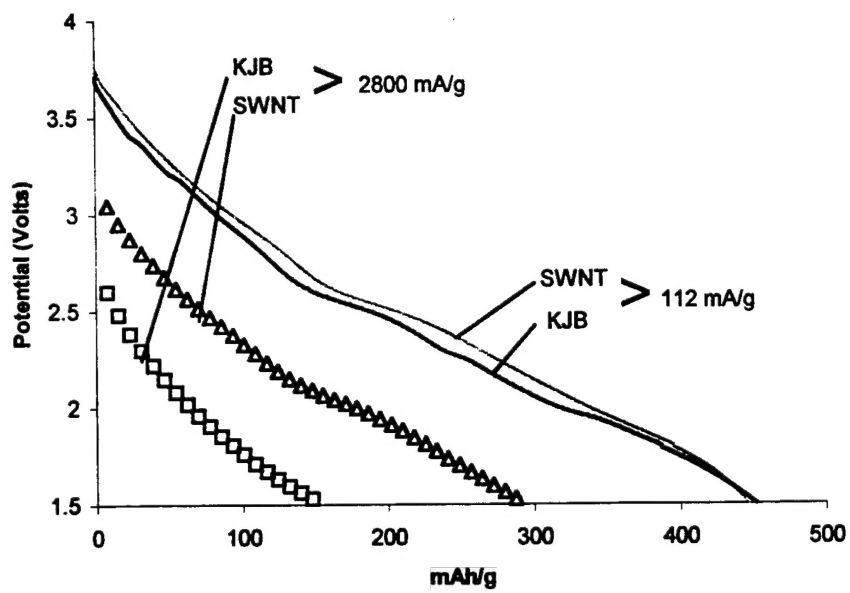
Figure 3. Galvanostatic discharge curves for V_2O_5/KJB (17 wt%) and V_2O_5/SWNT (17 wt%) composite electrodes discharged at 112 and 2800 mA/g.

Figure 4. Specific capacity as a function of specific current for intercalation electrodes containing V_2O_5 aerogels: (O) V_2O_5/SWNT (9 wt%); (X) V_2O_5/SWNT (17 wt%); (Δ) V_2O_5/KJB (17 wt%) electrodes.

Figure 5. Cycling data for three cells containing the V_2O_5/SWNT (17 wt%) composite electrode. The cells were discharged at 560 mA/g and charged at 280 mA/g between 4 and 1.5 V.

a.

b.

c.

Figure 1. TEM images for the following materials: (a) vanadium oxide ambigel; (b) SWNT's; (c) V_2O_5/SWNT composite electrode.

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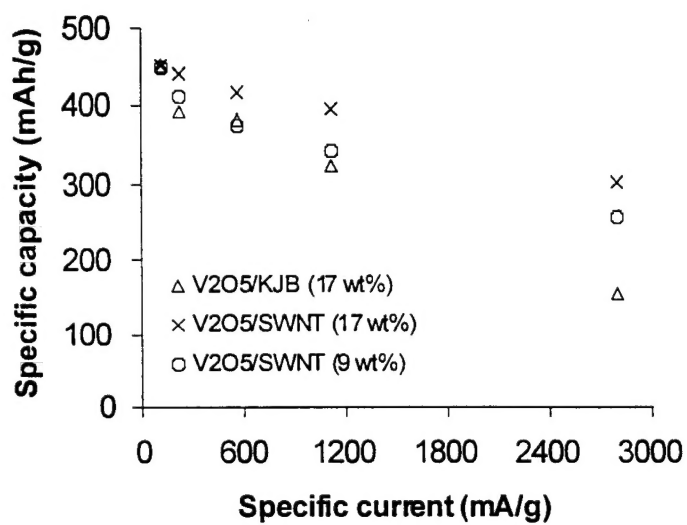
Figure 4. Specific capacity as a function of specific current for intercalation electrodes containing V_2O_5 aerogels: (O) V_2O_5/SWNT (9 wt%); (X)V_2O_5/SWNT (17 wt%); (Δ) V_2O_5/KJB (17 wt%) electrodes.
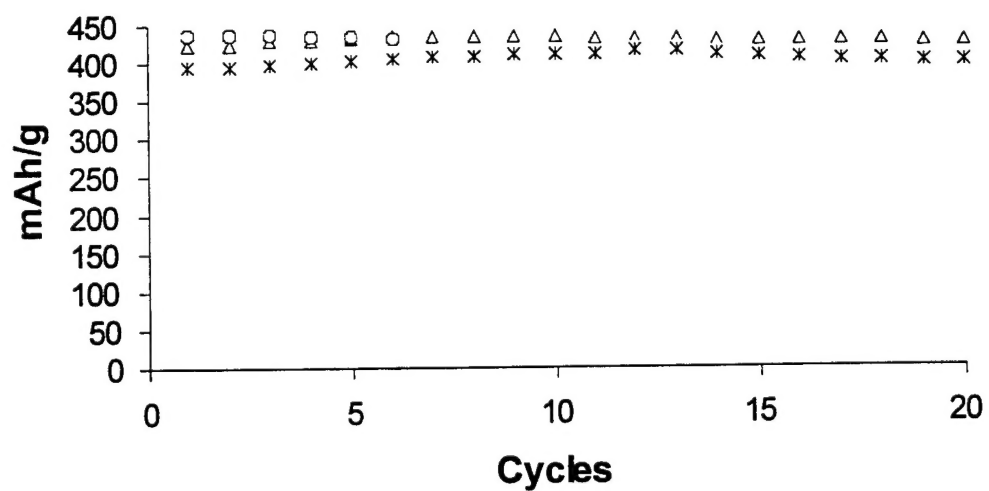
Figure 5. Cycling data for three cells containing the V_2O_5/SWNT (17 wt%) composite electrode. The cells were discharged at 560 mA/g and charged at 280 mA/g between 4 and 1.5 V.